A liquid-state theory that remains successful in the critical region

D. Pini; G. Stell; N. B. Wilding

Online Publication Date: 20 October 1998

To cite this Article: Pini, D., Stell, G. and Wilding, N. B. (1998) 'A liquid-state theory that remains successful in the critical region', Molecular Physics, 95:3, 483 - 494

To link to this article: DOI: 10.1080/002689798166828

URL: http://dx.doi.org/10.1080/002689798166828
A liquid-state theory that remains successful in the critical region

By D. PINI¹, G. STELL¹ and N. B. WILDING²

¹ Department of Chemistry, State University of New York at Stony Brook, Stony Brook, NY 11794-3400, USA
² Department of Physics and Astronomy, University of Edinburgh, Edinburgh EH9 3JZ, UK

(Received 20 January 1998; accepted 1 April 1998)

A thermodynamically self-consistent Ornstein–Zernike approximaton (SCOZA) is applied to a fluid of spherical particles with a pair potential given by a hard core repulsion and a Yukawa attractive tail

\[ w(r) = -\exp\left( -\frac{z(r-1)}{r} \right) \]  

This potential allows one to take advantage of the known analytical properties of the solution of the Ornstein–Zernike equation for the case in which the direct correlation function outside the repulsive core is given by a linear combination of two Yukawa tails and the radial distribution function \( g(r) \) satisfies the exact core condition \( g(r) = 0 \) for \( r < 1 \). The predictions for thermodynamics, the critical point, and the coexistence curve are compared with other theories and with simulation results. In order to assess unambiguously the ability of the SCOZA to locate the critical point and the phase boundary of the system, a new set of simulations also has been performed. The method adopted combines Monte Carlo and finite-size scaling techniques, and is especially adapted to deal with critical fluctuations and phase separation. It is found that the version of the SCOZA considered here provides very good overall thermodynamics and remarkably accurate critical point and coexistence curve. For the interaction range considered here, given by \( z = 1.8 \), the critical density and temperature predicted by the theory agree with the simulation results to about 0.6%.

1. Introduction

After applying their version of thermodynamic perturbation theory to square-well and Lennard-Jones fluids, John Barker and Doug Henderson characterized it as a 'successful theory of liquids' [1] and so it was. When tested against simulation results it proved to be impressively accurate at liquid-state densities and temperatures, unlike some versions of thermodynamic perturbation theory that had preceded it. Additionally, it bypassed the troubling lack of thermodynamic self-consistency associated with the direct use of the radial distribution functions obtained from the integral equation theories then available, as well as yielding thermodynamic results as good as or better than the best results obtainable from such integral equations.

These positive features became hallmarks of successful thermodynamic perturbation theories for simple fluids and were shared by the versions [2] that followed the Barker and Henderson work and by an alternative perturbative approach set forth somewhat earlier by Hauge and Hemmer [3] that was based on using the inverse range of the attractive interaction rather than its strength as a perturbation parameter. Integral equation approaches with improved self-consistency were developed subsequently to yield accurate liquid-state thermodynamics [4].

Unfortunately, the accuracy of all these approaches begins to decrease substantially as one leaves the liquid-state region located slightly above the triple point in temperature and follows the liquid–gas coexistence curve in the density–temperature plane up to the critical region. In particular, the shape of the coexistence curve and location of the critical point are not reproduced accurately, and nor are related critical parameters. In the case of the perturbation theories, it is not hard to understand why this is so. All of them are mean-field-like in nature, associated with coexistence curves that are quadratic close to the critical point, whereas the true coexistence curve is very nearly cubic. That is, in these theories one finds near the critical point a coexistence curve of the form

\[ T_c - T \approx A |\rho - \rho_c|^x \quad x = 2 \quad (1) \]

where \( \rho_c \) and \( T_c \) are the critical values of number density \( \rho \) and absolute temperature \( T \), and \( A \) is a constant. In contrast, in an exact treatment, one would expect to find \( x \) close to 3. In these theories the resulting \( T_c \) usually is more than 5% too high and the critical compressibility factor \( (p / \rho k_B T)_c \) usually is more than 10% too high. Here \( p \) is the pressure, and \( k_B \) is the Boltzmann constant.
The thermodynamics associated with the radial distribution function $g(r)$ obtained from various integral equation approaches cannot be categorized so neatly. However, in the cases in which there are substantial discrepancies between the several paths available for obtaining thermodynamics from $g(r)$ often the most reliable and accurate coexistence behaviour is obtained from evaluating the thermodynamics through the excess internal energy expressed in terms of an integral over the pair potential $w(r)$ weighted by $g(r)$. For continuum-fluid models the resulting critical behaviour is typically mean-field like in the cases that we have studied, and thus subject to the same deficiencies as one approaches the critical region. In some integral equation approaches that have been developed in order to ensure a certain degree of thermodynamic consistency, the description of the critical region and of the phase diagram appears to be more problematic: for instance, the modified hypernetted chain (MHNC) theory [5] is indeed able to predict quite satisfactorily the liquid and the vapour branches of the coexistence curve of a simple fluid at low enough temperatures, but it fails to converge close to the critical point, so that the two branches remain unconnected, and the position of the critical point is not given directly by the theory, but must be determined by extrapolation [6, 7]. The same kind of behaviour [6, 8] is found also for the HMSA integral equation (the acronym coming from the fact that the theory [9] interpolates between the hypernetted chain (HNC) and the soft mean spherical approximation (SMSA)).

The self-consistent Ornstein–Zernike approximation (SCOZA) we consider here is not mean-field-like, and it remains highly accurate as one goes from liquid-state conditions to critical point conditions. In particular the power $x$ in equation (1) recently was shown analytically to be given in the SCOZA by exactly 20/7 [10]. Also, as we discuss in this paper, in the hard core Yukawa fluid (HCYF) $r_c$ appears to be within 0.6% of its value as estimated by our simulation results. (Similarly, in recent three-dimensional lattice–gas studies [11, 12] the SCOZA $r_c$ was found to be within 0.2% of its estimated exact value.) As described in section 3, the scaling behaviour of the SCOZA thermodynamics is somewhat different from the simple scaling one expects to see in the exact thermodynamics, although those differences begin to appear clearly only when $\rho$ and $\tau$ are within 1% of their critical values. Closer to the critical point, the effective exponents defined above $r_c$ approach spherical-model values as the critical point is approached, whereas the exponents defined below $r_c$ do not.

The SCOZA was proposed some time ago by Hoye and Stell [13, 14] but fast and accurate algorithms for evaluating its thermodynamic predictions were developed only recently [11, 12, 15]. A sharp assessment of its accuracy for the HCYF could not be made on the basis of existing simulations, and for that reason our study here includes new Monte Carlo (MC) results exploiting finite-size scaling (FSS) techniques [16].

We have chosen the HCYF pair potential as the first of the continuum-fluid potentials to be considered in our studies of the SCOZA for several reasons. First, it embodies the two key features one requires in an off-lattice pair potential in order to consider both the liquid state and liquid–gas criticality: a highly repulsive core and an attractive well. Second, analysing the HCYF proves to be particularly convenient using the SCOZA (the square-well fluid is far less convenient in this regard). Third, the functional form of the hard core Yukawa potential makes it appropriate as a generic solvent-averaged interaction potential between polyelectrolyte or colloidal particles and as a generic simple-fluid pair potential. For this reason it seems particularly useful to have an accurate theory for both the structure and thermodynamics of the HCYF, which has already been the subject of a number of previous studies. We shall make contact with several of those here.

This paper is organized as follows: in section 2 we describe the theory and present some details of the method for the system under study, in section 3 our results are shown and a comparison with other theories and simulation results is made, and in section 4 our conclusions are drawn. The treatment of the hard sphere gas and the main features of the MC-FSS simulation method are summarized respectively in Appendix A and Appendix B.

2. Theory

Here we consider a fluid of spherical particles interacting via a two-body potential $v(r)$ which is the sum of a singular repulsive hard sphere contribution and an attractive tail $w(r) < 0$. The expression for $v(r)$ is then

$$v(r) = \begin{cases} +\infty & r < 1, \\ w(r) & r > 1, \end{cases}$$

(2)

where the hard sphere diameter $\sigma$ has been set equal to unity. As is customary in integral equation theories of fluids, the present approach introduces an approximate closure relation for the direct correlation function $c(r)$ which, once supplemented with the exact Ornstein–Zernike equation involving $c(r)$ and the radial distribution function $g(r)$, yields a closed theory for the thermodynamics and the correlations of the system under study. The basic requirement we want to incorporate in the SCOZA is the consistency between the compressibility and internal energy route to the thermodynamics. According to the compressibility route, the thermo-
dynamics stems from the reduced compressibility $\chi_{\text{red}}$ as determined by the sum rule

$$\chi_{\text{red}} = \frac{1}{1 - \rho \hat{c}(k = 0)}, \tag{3}$$

where $\hat{c}(k)$ is the Fourier transform of the direct correlation function and $\rho$ is the number density of the system. In the internal energy route the key to the thermodynamics is provided instead by the excess internal energy as given by the integral of the interaction weighted by the radial distribution function:

$$u = 2\pi \rho^3 \int_1^{\infty} dr^2 w(r) g(r), \tag{4}$$

where $u$ is the excess internal energy per unit volume and we have taken into account that $g(r)$ vanishes for $r < 1$ due to the hard core repulsion. In the following we will refer to the ‘excess internal energy’ simply as the ‘internal energy’. If $\chi_{\text{red}}$ and $u$ come from a unique Helmholtz free energy it is straightforward to find that one must have

$$\frac{\partial}{\partial \beta} \left( \frac{1}{\chi_{\text{red}}} \right) = \rho \frac{\partial^2 u}{\partial \rho^2}, \tag{5}$$

where $\beta = 1/(k_B T)$, $T$ being the absolute temperature, and $k_B$ the Boltzmann constant. While this relation is of course satisfied by the exact compressibility and internal energy, this is not the case with those predicted by most integral equation theories. In order to cope with this lack of thermodynamic consistency, we consider the following closure to the Ornstein–Zernike equation:

$$\begin{cases} g(r) = 0 & r < 1 \\ c(r) = c_{\text{HS}}(r) + \kappa (\rho, \beta) w(r) & r > 1, \end{cases} \tag{6}$$

where $c_{\text{HS}}(r)$ is the direct correlation function of the hard sphere fluid, and $\kappa (\rho, \beta)$ is a function of the thermodynamic state of the system. In equation (6) the approximation clearly lies in the simple form of $c(r)$ outside the repulsive core. The closure above resembles the one used in the approximation known as both the lowest-order gamma-ordered approximation (LOGA) [17] and the optimized random phase approximation (ORPA) [18]. However, whereas in the LOGA/ORPA one has $\kappa (\rho, \beta) \equiv - \beta$, in equation (6) $\kappa (\rho, \beta)$ is not fixed a priori, but instead must be determined so that thermodynamic consistency condition (5) is satisfied. This gives rise to a partial differential equation (PDE) for the function $\kappa (\rho, \beta)$, provided that an expression for the hard sphere direct correlation function $c_{\text{HS}}(r)$ is given. The most popular parameterization for $c_{\text{HS}}(r)$ in the fluid region is due to Verlet and Weis [19]. Another choice that yields the same thermodynamics as Verlet–Weis, and that we find convenient in view of the calculations performed in this work, is originally due to Waisman [20] It was subsequently extended analytically by Hoye and Stell [21] and explored in some detail by Henderson and coworkers [22]. It amounts to assuming that the function $c_{\text{HS}}(r)$ outside the repulsive core has a one-Yukawa form, so that for the hard sphere system we have

$$\begin{cases} g_{\text{HS}}(r) = 0 & r < 1 \\ c_{\text{HS}}(r) = \kappa_1 \exp \left[ - z_1 (r - 1) \right] & r > 1, \end{cases} \tag{7}$$

The Ornstein–Zernike equation supplemented by equation (7) can be solved analytically in terms of the amplitude $\kappa_1$ and the inverse range $z_1$ of $c_{\text{HS}}(r)$. In turn these can be determined as a function of the density by requiring, as in the Verlet–Weis parameterization, that both the compressibility and the virial route to the thermodynamics give the Carnahan–Starling equation of state. The basic features of the calculation are recalled in appendix A.

A considerable, although purely technical, simplification in the closure scheme outlined above based on equations (5) and (6) occurs when also the attractive potential $w(r)$ in equation (2) is given by a Yukawa function, i.e., when one has

$$w(r) = - \exp \left[ - z(r - 1) \right], \tag{8}$$

where $z$ is the inverse range of the potential and the interaction strength $\varepsilon$ has been set equal to one. In the following, the density $\rho$ and the temperature $T$ will be expressed in units of $\sigma^{-3}$ and $\varepsilon/k_B$ respectively, so we will identify them with the usual reduced quantities $\rho^* = \rho \sigma^3$, $T^* = k_B T / \varepsilon$. From equation (7) it is seen that equation (6) becomes

$$\begin{cases} g(r) = 0 & r < 1 \\ c(r) = \kappa_1 \exp \left[ - z_1 (r - 1) \right] + \kappa_2 \exp \left[ - z_2 (r - 1) \right] & r > 1, \end{cases} \tag{9}$$

where $\kappa_2$ and $z_2$ are the quantities referred to as $\kappa$ and $z$ in equations (6) and (8), and $\kappa_1, z_1$ are known functions of the density. It is now possible to take advantage of the fact that for the Ornstein–Zernike equation supplemented by closure (9) extensive analytical results have been determined [23, 24, 14] If both $\kappa_1$ and $\kappa_2$ are given, as in the LOGA/ORPA, this enables one to solve equation (9) altogether [25–27] More generally, irrespective of the form of $\kappa_1$ and $\kappa_2$, a prescription can be found to determine the reduced compressibility $\chi_{\text{red}}$ as a function of the density $\rho$ and the internal energy per unit volume $u$, which can be used in equation (5) to obtain a closed PDE. A similar procedure for the
same potential considered here was adopted in a previous work \[15\] but with \( \epsilon(r) \) given outside the core by a single Yukawa term. In its simplest version \[13\] this term is proportional to the pair potential. This further simplifies the theory, but implies that the description of the hard sphere fluid coincides with that of the Percus–Yevick (PY) approximation which, as is well known, is not very satisfactory at high densities. This defect becomes more and more severe as the range of the attractive interaction decreases, and can considerably affect the phase diagram predicted by the theory even at the relatively low density of the critical point, unless some procedure is adopted to correct the hard sphere thermodynamics, such as having the magnitude of the Yukawa term reduced at \( r = \infty \) to a value that yields Carnahan–Starling thermodynamics, instead of vanishing. This gives rise to the one-Yukawa theory that was reported in \[15\] which is found to be fully satisfactory thermodynamically, but does not incorporate the hard sphere contribution to \( \epsilon(r) \) accurately outside the core. Alternatively, in order to include a better treatment of the hard sphere fluid in the theory one can turn to the two-Yukawa form for \( \epsilon(r) \) of equation (9), whose use in consistency condition (5) we shall now illustrate in some detail. In the following we shall exploit the results determined in [23, 24, 14]. Let us introduce the packing fraction \( \xi = \pi \rho / 6 \) and the quantity

\[
\gamma = (1 - \xi)(1 + \xi) \frac{1}{2},
\]

which is the square root of the quantity referred to as \( \chi \) in \[23, 24, 14\] Equation (5) becomes

\[
\frac{2\gamma}{(1 - \xi)^{3/2}} \left( \frac{\partial}{\partial u} \right) \rho = \frac{\rho (\partial u)}{\partial \rho} \left( \frac{\partial}{\partial \rho} \right) \beta.
\]

To obtain a PDE for \( u \) we need to express \( \gamma \) as a function of \( \rho \) and \( u \) in equation (11). From \[24\] equation (14) it is found that \( \gamma \) can be written as

\[
\gamma = -\frac{2 + 4\gamma_{1/2}(\gamma_{2} - \gamma_{1})}{4(\gamma_{1} + \gamma_{2})\gamma_{2} - (\gamma_{1} + \gamma_{2})\gamma_{1}} - \frac{z_{1}z_{2}}{z_{1} + z_{2}} \frac{\gamma_{1}\gamma_{2}(\gamma_{2} - \gamma_{1})}{[\gamma_{1} + \gamma_{2}]\gamma_{2} - (\gamma_{1} + \gamma_{2})\gamma_{1}},
\]

where we have set

\[
g = \frac{(1 + 2\xi)^{2}}{(1 - \xi)^{2}}.
\]

The quantities \( \gamma_{1} \) and \( \gamma_{2} \) are given by \[24\] equation (5)

\[
\gamma_{1} = 2 - g^{1/2} - \frac{U_{1}}{U_{0}},
\]

\[
\gamma_{2} = 2 - g^{1/2} - \frac{W_{1}}{W_{0}}.
\]

The ratios \( U_{1}/U_{0} \) and \( W_{1}/W_{0} \) depend on the integrals

\[
i_{i} = 4\pi \int_{0}^{\infty} dr \exp \left( -1 \right), i = 1, 2.
\]

From \[23\] equation (35) it is found in fact that

\[
\frac{W_{1}}{W_{0}} = \frac{4 + 2z_{2} - z_{2}^{2} \tau_{1} \tau_{2} - 1}{2(2 + z_{2}) \sigma_{2} \tau_{2} - 1},
\]

and the corresponding relation with \( W_{1}/W_{0} \) replaced by \( U_{1}/U_{0} \) and the index 2 changed to 1. The quantities \( \tau_{1} \) and \( \sigma_{1} \) depend only on \( z_{1} \) and are given by \[23\] equation (34):

\[
\tau_{1} = \frac{1}{2z_{1}} \left[ \frac{z_{1} - \frac{1}{2}}{z_{1} + \frac{1}{2}} + \exp \left( -z_{1} \right) \right],
\]

\[
\tau_{2} = \frac{1}{2z_{2}} \left[ \frac{z_{2} + 2}{4 + 2z_{2} - z_{2}^{2}} + \exp \left( -z_{2} \right) \right],
\]

with \( i = 1, 2 \). From the expression of the potential (equation (8)) it is seen that \( \tau_{2} \) is directly related to the internal energy per unit volume \( u \) given by equation (4):

\[
u = -\frac{1}{2} \rho \tau_{2}.
\]

Equations (15), (17) and (20) let us express \( \gamma_{2} \) explicitly as a function of \( \rho \) and \( u \):

\[
\gamma_{2} = 2 - g^{1/2} - \frac{4 + 2z_{2} - z_{2}^{2} \tau_{1} \rho + \rho}{2(2 + z_{2}) \sigma_{2} \tau_{2} + \rho}.
\]

We now need \( \gamma_{1} \) as a function of \( \rho \) and \( u \). This is less straightforward than for \( \gamma_{2} \), since the integral \( i_{1} \) does not have any direct thermodynamic meaning, the exponential in \( \gamma_{1} \) being related to the tail of the direct correlation function of the hard sphere gas. We have then to make use of some further results determined in \[23, 24, 14\]. From \[23\] equation (36), it is found that the amplitudes \( \kappa_{1}, \kappa_{2} \) of the Yukawa functions in closure (9) can be expressed in terms of the above introduced quantities \( U_{0}, U_{1}, W_{0}, W_{1} \). One has

\[
\kappa_{1} = \frac{2(\gamma_{1} + 2)^{2} \sigma_{2}^{2}}{3 \xi^{2} \gamma_{1}} U_{0} \left[ \frac{u}{u_{0}} - \alpha_{1} \right]^{2},
\]

where \( \alpha_{1} \) is given by \[23\] equation (37):

\[
\alpha_{1} = \frac{(4 + 2z_{1} - z_{1}^{2}) \tau_{1}}{2(2 + z_{1}) \sigma_{1}};
\]

and the corresponding equations with the index 1 replaced by 2 and \( U_{0}, U_{1} \) replaced by \( W_{0}, W_{1} \). Let us now introduce the quantities \( x, y \) given by
\[ x = q^{1/2} - \frac{z_1}{4\gamma_1}, \quad (24) \]
\[ y = q^{1/2} - \frac{z_2}{4\gamma_2}. \quad (25) \]

From [14] equation (30), one has
\[ u_0 = \frac{4}{z_1} \rho (q^{1/2} - x)^2, \quad (26) \]
\[ w_0 = \frac{4}{z_2} \rho (q^{1/2} - y)^2. \quad (27) \]

where \( \rho \) and \( s \) must satisfy [24] equation (39) (in the notation of [24] one has \( x = u_{x1}/u_{x0} \), \( y = w_{x1}/w_{x0} \), \( \rho \equiv u_{y0} \), \( s \equiv w_{y0} \):
\[
\rho + s + \frac{4x}{z_1^2 - z_2^2} (y - x)^2 = \frac{1}{4} z_1^2 - x^2, \\
\rho + s - \frac{4x}{z_1^2 - z_2^2} (y - x)^2 = \frac{1}{4} z_2^2 - y^2. \quad (28)
\]

Equation (28) is readily solved for \( \rho \) and \( s \) to give
\[
\rho = -\frac{z_1^2 - z_2^2}{64 (y - x)^4} \left\{ 4 z_2^2 (y - x)^2 - 16 \delta^2 (y - x)^2 \\
- (z_1^2 - z_2^2) \left[ \frac{1}{4} z_1^2 + 4 (y^2 - x^2) \right] \right\}, \quad (29)
\]
and the expression for \( s \) is obtained by exchanging \( z_1, z_2 \) and \( x, y \) in the RHS of equation (29). If equations (14), (24), (26), (29) are used in (22) we obtain finally
\[
\begin{aligned}
&\left[ (2 - q^{1/2} - \alpha_t) (q^{1/2} - x) - \frac{1}{z_1} \left\{ 4 z_2^2 (y - x)^2 - 16 \delta^2 (y - x)^2 \\
&- (z_1^2 - z_2^2) \left[ \frac{1}{4} z_1^2 + 4 (y^2 - x^2) \right] \right\} \right] \\
&= -\frac{384 \delta^4 z_2^2}{(z_1 + 2) (z_1^2 - z_2^2) \alpha_t} K_1 (y - x)^4, \quad (30)
\end{aligned}
\]

and a similar equation obtained by exchanging the indices 1 and 2 and the quantities \( x, y \).

We recall that in equation (30) \( K_1, z_1, \sigma_1, \) and \( \alpha_t \) are known functions of the density \( \rho \) which refer to the hard sphere system. For given values of \( \rho \) and \( u \), equations (21) and (25) allow one to determine \( y \). Equation (30) then can be solved numerically with respect to \( \rho \) to obtain \( \gamma_1 \) via equation (24). This solves the problem of determining \( \gamma_1 \) in terms of \( \rho \) and \( u \). The partial derivative \((\partial\gamma_1/\partial u)_\rho\) that appears in equation (11) can then be determined as
\[
\left( \frac{\partial\gamma_1}{\partial u} \right)_\rho = \frac{\partial\gamma_1}{\partial u} \rho + \frac{\partial\gamma_2}{\partial u} \rho + \frac{\partial\gamma_3}{\partial u} \rho, \quad (31)
\]
where \((\partial\gamma_2/\partial u)_\rho\) is calculated explicitly by equation (21), while \((\partial\gamma_1/\partial u)_\rho\) must be determined as the derivative of the function implicitly defined by equation (30). If we write equation (30) as \( F(x, y, \rho) = 0 \), it is found straightforwardly that equation (11) takes the form
\[
B(\rho u) \frac{\partial u}{\partial \beta} = c(\rho u) \frac{\partial^2 u}{\partial \beta^2}, \quad (32)
\]
where the functions \( B(\rho u) \) and \( c(\rho u) \) are given by the following expressions:
\[
\begin{aligned}
B(\rho u) &= \frac{2i}{(1 - \xi^2)^2} \left[ \frac{\partial F}{\partial \gamma_1} \frac{\partial F}{\partial \gamma_2} - \frac{\partial F}{\partial \gamma_1} \frac{\partial F}{\partial \gamma_2} \frac{\partial F}{\partial \gamma_3} \right], \quad (33) \\
c(\rho u) &= \frac{\partial F}{\partial \gamma_1} \frac{\partial F}{\partial \gamma_2}. \quad (34)
\end{aligned}
\]

All the partial derivatives in equations (33) and (34) are calculated at constant \( \rho \) and can be determined by equations (12), (21), (24), (25), (30). The resulting expressions then are evaluated as functions of \( \rho \) and \( u \) via the procedure described above. The same procedure also allows one to determine the reduced compressibility as \( 1/\chi_{\text{red}} = s^2/(1 - \xi^2) \) once \( s \) has been obtained from equation (12). PDE (32) is a nonlinear diffusion equation that must be integrated numerically. To prevent the occurrence of any numerical instability, especially in the critical and sub-critical regions, we have adopted an implicit finite-differences algorithm [28] tailored to equation that, although globally nonlinear, depend on the partial derivatives of the unknown function in a linear fashion like equation (32). The integration with respect to \( \beta \) starts at \( \beta = 0 \) and goes down to lower and lower temperatures. Before each integration step equation (30) is solved numerically and the coefficients \( B(\rho u), c(\rho u) \) are determined. The density \( \rho \) ranges in a finite interval \( (0, \rho_0) \), whose high density boundary has been typically set at \( \rho_0 = 1 \). The initial condition can be determined by taking into account that at \( \beta = 0 \) the radial distribution function coincides with that of the hard sphere gas. From equations (4) and (8) one has then
\[
u(\rho, \beta = 0) = -2\pi \rho^2 \int_{-\infty}^{+\infty} dr \exp \left\{ z_2 (r - 1) \right\} \}, \quad (35)
\]
for every \( \rho \),
need two boundary conditions at $\rho = 0$ and $\rho = \rho_0$. From equation (4) one has immediately
\[ u(\rho = 0, \beta) = 0 \quad \text{for every } \beta. \] (36)

At high densities we instead make use of the so-called high temperature approximation (HTA), according to which the excess Helmholtz free energy per unit volume is determined via equation (35) for every temperature. In the fluid region of the phase diagram this of course is not exact unless $\beta = 0$, but it becomes more and more accurate as the density of the system is increased [29] so we expect that for a given sweep along the $\beta$ axis the results will not differ appreciably from those that would be obtained using a hypothetical exact boundary condition, provided that the boundary $\rho_0$ is located at sufficiently high density. We used the HTA at $\rho = \rho_0$ for the reduced compressibility. This yields via equation (5) the boundary condition
\[ \bar{\partial}_u^2 \bar{\partial}_\rho^2 (\rho_0, \beta) = \bar{\partial}_u^2 (\rho_0, \beta = 0) \quad \text{for every } \beta. \] (37)

We have checked that the output of the numerical integration of equation (32) is quite insensitive to the specific choice of the high density boundary condition. Moreover, for $\rho_0 \approx 1$ moving the boundary condition to higher densities also leaves the results unaffected. Equation (10) shows that, in order to be meaningful, the quantity $f$ has to be non-negative. On the other hand, below the critical temperature the solution of equation (32) does not satisfy this condition along the whole density interval $(0, \rho_0)$. Instead, there is a certain temperature-dependent region $(\rho_0(1), \rho_0(2))$ such that $f$ becomes negative as soon as $\rho$ becomes larger than $\rho_0(1)$ or smaller than $\rho_0(2)$. For $\rho = \rho_0(1)$ or $\rho = \rho_0(2)$ the quantity $f$ vanishes and, consequently, the compressibility diverges. As $\beta$ changes, $\rho_0(1)$ and $\rho_0(2)$ give then, respectively, the low and the high density branch of the spinodal curve predicted by the theory. The fact that $f$ becomes negative when $\rho$ crosses the spinodal curve not only implies that the theory behaves unphysically for these values of $\rho$ but also it gives rise to an analytical instability which would make the numerical integration of PDE (32) impossible, if one tried to determine the solution over the whole interval $(0, \rho_0)$ even below the critical temperature. Therefore, the region bounded by the spinodal has been excluded from the integration of equation (32). Specifically, as soon as it is found that $f$ changes sign, so that for a certain density $\tilde{\rho}$ one has $f(\tilde{\rho}, \beta) < 0$, the integration is restricted to the interval $(0, \tilde{\rho} - \Delta \rho)$ or $(\tilde{\rho} + \Delta \rho, \rho_0)$, respectively, for $\tilde{\rho} < \rho_c$ or $\tilde{\rho} > \rho_c$, where $\Delta \rho$ is the spacing of the density grid and $\rho_c$ is the critical density. Within the precision of the numerical discretization, one has $\rho_{s1} = \tilde{\rho} - \Delta \rho$ (or $\rho_{s2} = \tilde{\rho} + \Delta \rho$) and the further boundary conditions
\[ u(\rho_{s1}, \beta) = u_\rho(\rho_{s2}) \quad i = 1, 2, \quad \beta > \beta_c \] (38)
where $\beta_c$ is the critical inverse temperature and $u_\rho(\rho)$ is the value of the internal energy per unit volume when the compressibility at density $\rho$ diverges. This can be determined by setting $f = 0$ in equation (12) and solving for $\gamma_1$ as a function of $\rho$ and $\gamma_2$. If equations (24) and (25) are substituted into equation (30), an equation for $\gamma_2$ is obtained that allows one to determine the value of $\gamma_2$ when $1/\chi_{red} = 0$ for a certain $\rho$. Solving equation (21) with respect to $u$ then yields $u_\rho(\rho)$.

Once the internal energy per unit volume $u$ has been determined from equation (32), the pressure $p$ and the chemical potential $\mu$ are obtained by integration with respect to $\beta$ via the relations $\partial(\beta p)/\partial \beta = -u + \rho \partial u/\partial \rho$, $\partial(\beta u)/\partial \beta = \partial u/\partial \rho$. Thanks to the self-consistency of the theory, this route to the thermodynamics is equivalent to integrating the inverse compressibility with respect to $\rho$, but it does not require one to circumvent the forbidden region in order to reach the high density branch of the subcritical isotherms.

3. Results
The numerical integration of PDE (32) with initial condition (35) and boundary conditions (36)–(38) has been performed on a density grid with $\Delta \rho = 10^{-3} - 10^{-4}$. At the beginning of the integration the temperature step $\Delta \beta$ was usually set at $\Delta \beta = 2 \times 10^{-5} - 10^{-5}$. As the temperature approaches its critical value, $\Delta \beta$ can be decreased further if one wishes to get very close to the critical point, and then gradually expanded back. The integration was usually carried down to $\beta \approx 2.4 \beta_c$. The inverse range parameter of the attractive tail in equation (8) has been set at $z = 1.8$. For this value of $z$ several simulations [30–32] and theoretical [6, 26, 27] predictions have been reported in the literature. Figure 1 shows the SCOZA results for the compressibility factor $z = p/(\rho k_B T)$ along two different isotherms, corresponding to $r = 2$ and $r = 1.5$, together with the MC simulation results by Henderson and coworkers [30]. The agreement is very good both at low and high densities. The compressibility factors are reported also in table 1, together with those obtained by the LOGA/ORPA via the internal energy route [27] which is the one that gives the best agreement with the simulation results. It can be seen that for the non-critical states reported here the SCOZA and the energy route of the LOGA/ORPA are very close to each other. In table 2 the predictions for the chemical potential and the reduced compressibility are compared with the data from the MC simulations performed in this work. The internal energy per particle is reported in table 3, where
Table 1. Compressibility factor $\rho^* V/Nk_B T$ for the hard sphere $+$ Yukawa fluid ($\epsilon = 1.8$). Density and temperature are in reduced units $\rho^* = \rho \sigma^3$, $T^* = k_B T/\epsilon$, where $\sigma$ is the hard sphere diameter and $\epsilon$ is the strength of the attractive potential.

<table>
<thead>
<tr>
<th>$T^*$</th>
<th>$\rho^*$</th>
<th>MC$^a$</th>
<th>SCOZA</th>
<th>LOGA/ORPA$^b$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\infty$</td>
<td>0.4</td>
<td>2.52</td>
<td>2.518</td>
<td>2.518</td>
</tr>
<tr>
<td>$\infty$</td>
<td>0.6</td>
<td>4.22</td>
<td>4.283</td>
<td>4.283</td>
</tr>
<tr>
<td>$\infty$</td>
<td>0.8</td>
<td>7.65</td>
<td>7.750</td>
<td>7.750</td>
</tr>
<tr>
<td>2.0</td>
<td>0.4</td>
<td>1.08</td>
<td>1.120</td>
<td>1.118</td>
</tr>
<tr>
<td>2.0</td>
<td>0.6</td>
<td>2.04</td>
<td>1.977</td>
<td>1.974</td>
</tr>
<tr>
<td>2.0</td>
<td>0.8</td>
<td>4.27</td>
<td>4.433</td>
<td>4.432</td>
</tr>
<tr>
<td>1.5</td>
<td>0.4</td>
<td>0.69</td>
<td>0.667</td>
<td>0.663</td>
</tr>
<tr>
<td>1.5</td>
<td>0.6</td>
<td>1.21</td>
<td>1.220</td>
<td>1.214</td>
</tr>
<tr>
<td>1.5</td>
<td>0.8</td>
<td>3.31</td>
<td>3.333</td>
<td>3.330</td>
</tr>
</tbody>
</table>

$^a$ Monte Carlo data from [30] $^b$ LOGA/ORPA-energy route results from [27]

Table 2. Chemical potential $\mu$ and reduced compressibility $\chi_{red}$ of the hard sphere Yukawa fluid ($\epsilon = 1.8$). Density and temperature are in reduced units.

<table>
<thead>
<tr>
<th>$T^*$</th>
<th>$\rho^*$</th>
<th>MC$^a$</th>
<th>SCOZA</th>
<th>LOGA/ORPA$^b$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\infty$</td>
<td>0.4</td>
<td>1.736(2)</td>
<td>1.7316</td>
<td>0.1958(2)</td>
</tr>
<tr>
<td>$\infty$</td>
<td>0.6</td>
<td>4.833(2)</td>
<td>4.8147</td>
<td>0.0848(5)</td>
</tr>
<tr>
<td>2.0</td>
<td>0.4</td>
<td>-0.936(2)</td>
<td>-0.9396</td>
<td>0.4992(8)</td>
</tr>
<tr>
<td>2.0</td>
<td>0.6</td>
<td>0.515(2)</td>
<td>0.5003</td>
<td>0.1594(5)</td>
</tr>
<tr>
<td>1.5</td>
<td>0.4</td>
<td>-1.823(2)</td>
<td>-1.8258</td>
<td>0.968(3)</td>
</tr>
<tr>
<td>1.5</td>
<td>0.6</td>
<td>-0.905(2)</td>
<td>-0.9294</td>
<td>0.2217(5)</td>
</tr>
</tbody>
</table>

$^a$ Monte Carlo simulation performed in this work. The numbers in parentheses give the error in the last figure.

Table 3. Chemical potential $\mu$ and reduced compressibility $\chi_{red}$ of the hard sphere Yukawa fluid. All quantities are in reduced units.

<table>
<thead>
<tr>
<th>$T^*$</th>
<th>$\rho^*$</th>
<th>MC$^a$</th>
<th>SCOZA</th>
<th>LOGA/ORPA$^b$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\infty$</td>
<td>0.4</td>
<td>-2.495</td>
<td>-2.516(2)</td>
<td>-2.517</td>
</tr>
<tr>
<td>$\infty$</td>
<td>0.6</td>
<td>-3.975</td>
<td>-4.002(2)</td>
<td>-4.002</td>
</tr>
<tr>
<td>$\infty$</td>
<td>0.8</td>
<td>-5.573</td>
<td>-5.611</td>
<td>-5.611</td>
</tr>
<tr>
<td>2.0</td>
<td>0.4</td>
<td>-2.583</td>
<td>-2.595(2)</td>
<td>-2.583</td>
</tr>
<tr>
<td>2.0</td>
<td>0.6</td>
<td>-4.030</td>
<td>-4.036(2)</td>
<td>-4.030</td>
</tr>
<tr>
<td>2.0</td>
<td>0.8</td>
<td>-5.622</td>
<td>-5.620</td>
<td>-5.618</td>
</tr>
<tr>
<td>1.5</td>
<td>0.4</td>
<td>-2.622</td>
<td>-2.640(2)</td>
<td>-2.623</td>
</tr>
<tr>
<td>1.5</td>
<td>0.6</td>
<td>-4.051</td>
<td>-4.053(2)</td>
<td>-4.043</td>
</tr>
<tr>
<td>1.5</td>
<td>0.8</td>
<td>-5.630</td>
<td>-5.623</td>
<td>-5.621</td>
</tr>
<tr>
<td>1.0</td>
<td>0.6</td>
<td>-4.073</td>
<td>-4.097</td>
<td>-4.065</td>
</tr>
<tr>
<td>1.0</td>
<td>0.8</td>
<td>-5.635</td>
<td>-5.631</td>
<td>-5.628</td>
</tr>
</tbody>
</table>

$^a$ Monte Carlo simulation of [30] $^b$ Monte Carlo simulation performed in this work. The numbers in parentheses give the error in the last figure.

Figures 1-3. \(\mu^*/k_B T\) as a function of reduced density $\rho^*$ for the hard sphere $+$ Yukawa fluid for two isotherms at reduced temperatures $T^* = 2$ (upper curve) and $T^* = 1.5$ (lower curve). The critical point predicted by the theory has been located by the vanishing of the inverse compressibility $1/\chi_{red}$. No extrapolation procedure to $1/\chi_{red} = 0$ is necessary, since the algorithm adopted here allows one to get as close as desired to the critical singularity. As mentioned in section 2, below the critical temperature $T_c$ the theory yields a spinodal curve. The coexistence curve must be determined by a Maxwell construction, i.e., by imposing the equilibrium conditions $\mu(\rho_g, T^*) = \mu(\rho_l, T^*)$, $P(\rho_g, T^*) = P(\rho_l, T^*)$ for the densities $\rho_g, \rho_l$ of the gas and liquid phases at coexistence at a temperature $T^*$. In comparing our results for the critical point and the coexistence curve with the available simulation data, we found that the two simulations for the phase diagram of the system under study already reported in the literature [31, 32] do not agree very well with each other. We then performed a new set of simulations using the MC-FSS method summarized in appendix B. The SCOZA and the simulation results for the critical point are compared in table 4, which shows also the predictions of other theories [6]. It can be seen that the agreement between the SCOZA and the present simulation is remarkably good; the errors in the critical density $\rho_c$ and temperature $T_c$ are, respectively, slightly more and slightly less than 0.6%. The SCOZA and the simulation coexistence curve in the temperature–density plane are compared in figure 2. Similar comparisons in the temperature–internal energy and in the temperature–chemical potential plane are shown, respectively, in figures 3 and 4. In every case the SCOZA agrees very well with the simulation. It should be noted that in the SCOZA the coexistence curve extends up to the critical point where, as
already observed in section 1, this is not always the case with other theories. In table 4 and figures 2–4 we have also reported the predictions of the simpler version of the SCOZA mentioned in section 2, in which the direct correlation function outside the repulsive core is given by just one Yukawa tail that vanishes as \( r \to \infty \), so that the resulting hard sphere gas is described in the PY approximation. We find that the treatment of the repulsive contribution considerably affects the phase diagram predicted by the theory, with the two-Yukawa SCOZA locating the critical point far more accurately than the one-Yukawa theory that reduces to the hard sphere PY approximation at \( r = \infty \). On the other hand, the one-Yukawa version of the SCOZA reported in [15] in which the Yukawa magnitude adjusts itself to give Carnahan-Starling hard sphere thermodynamics at infinite \( r \) is almost indistinguishable thermodynamically from the two-Yukawa theory reported here. (Its critical values

Table 4. Critical density and temperature (in reduced units) for the hard-sphere Yukawa fluid.

<table>
<thead>
<tr>
<th></th>
<th>MC'</th>
<th>MC''</th>
<th>MC'</th>
<th>SCOZA1-Yuk</th>
<th>SCOZA</th>
<th>HMSA'</th>
<th>MHNC'</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \rho^* )</td>
<td>0.294</td>
<td>0.313</td>
<td>0.312(2)</td>
<td>0.308</td>
<td>0.314</td>
<td>0.36</td>
<td>0.28</td>
</tr>
<tr>
<td>( T^* )</td>
<td>1.192</td>
<td>1.178</td>
<td>1.212(2)</td>
<td>1.201</td>
<td>1.219</td>
<td>1.25</td>
<td>1.21</td>
</tr>
</tbody>
</table>

\( ^\prime \) MC simulation of [31]
\( ^\prime \prime \) MC simulation of [32]
\( ^\prime \) MC simulation performed in this work.
\( ^\prime \) SCOZA with one-Yukawa \( \epsilon(r) \) (see text).
\( ^\prime \prime \) From [6]

Figure 2. Coexistence curve of the hard sphere Yukawa fluid \((\varepsilon = 1.8)\) in the density–temperature plane (density and temperature are in reduced units); full curve, SCOZA; dashed curve, SCOZA with a one-Yukawa direct correlation function \( \epsilon(r) \) (see text); and squares, MC results (this work).

Figure 3. Coexistence curve of the hard sphere Yukawa fluid in the internal energy–temperature plane. \( E^*/N \) is the internal energy per particle in reduced units. Notation as for figure 2.

Figure 4. Coexistence curve of the hard sphere Yukawa fluid in the temperature–chemical potential plane. All quantities are in reduced units. Notation as for figure 2.
The behaviour of the SCOZA in the critical region has been studied both analytically [10] and numerically [12] by two of us in a collaboration with Johan Høye. This investigation has shown that above the critical temperature the SCOZA yields the same critical exponents as the mean spherical approximation (MSA), i.e., $\gamma = 2$, $\delta = 5$, $\alpha = -1$, where the usual notation for the critical exponents has been used. On the other hand, on the coexistence curve the critical exponents are neither spherical nor classical, and one finds $\gamma' = 7/5$, $\alpha' = -1/10$, $\beta = 7/20$ (here of course $\beta$ is the critical exponent that gives the curvature of the coexistence curve near the critical point). The exponent $\eta$ given by the SCOZA is zero due to the Ornstein–Zernike approximation. We note that the standard algebraic relations among the critical exponents are satisfied both above and below $\tau_c$.

The different behaviour above and below the critical temperature can be traced back to the form of the equation of state which stems from PDE (32) in the critical region. Above the critical temperature the quantity $f$ defined in equation (10), which is proportional to $\chi_\text{red}^{-1/2}$ (and also to the inverse correlation length $\kappa$) behaves like

$$f_+ \approx a (\rho - \rho_c)^2 + b \tau + \ldots, \quad a, b > 0,$$

where $\tau = (\tau - \tau_c)/\tau_c$ is the reduced temperature, $f_+$ refers to $\tau > \tau_c$ and the $\approx$ refers to additional terms that do not play an active role in determining the exponents. Equation (39) gives rise to the scaling behaviour typical of MSA, and more generally of a wide class of Ornstein–Zernike theories which incorporate the requirement that $g(\cdot)$ must vanish for short distances due to the interparticle repulsion [33]. Below the critical temperature, on the other hand, the expression for $f$ predicted by the SCOZA, denoted by $f_-$, is given by

$$f_- \approx a (\rho - \rho_c)^2 + b \tau \left| \frac{\rho - \rho_c}{|\tau|^1/4} \right| + \ldots,$$

where the argument $z = |\rho - \rho_c|/|\tau|^{1/4}$ of the function $\psi$ is characteristic of Gaussian model scaling. For $z \to \infty$ one has $\psi(z) \to 1$, $\psi(z) \sim \exp (-\alpha z^4)$, $\alpha > 0$. This ensures that on the critical isotherm the two branches (39) and (40) and all their derivatives join smoothly, thereby preventing the occurrence of artificial singularities in the equation of state when the critical isotherm is crossed as $\rho \neq \rho_c$. Such an analytical transition away from the critical isochore is to be expected, since PDE (32) describes a nonlinear diffusion process in the temperature–density plane which must go on regularly as long as the diffusion coefficient $D = D (\rho, \tau)$ stays regular. This is true until the spinodal curve is reached.

On the spinodal the diffusion coefficient diverges, so this curve represents a locus of singular points. Its shape in the critical region can be determined from equation (40) in the limit $z \to 0$. One has then $\psi(z) \sim z$, which gives for the density on the spinodal curve $|\rho - \rho_c| \sim |\tau|^{1/4}$. We observe that equation (40) cannot be extended inside the spinodal to give a regular solution over the whole density axis, since it fails to be differentiable for $\rho = \rho_c$. This, however, does not affect the smoothness of $f_-$ in the region where it represents a meaningful solution of the SCOZA PDE. From the knowledge of $f_-$, the critical behaviour below $\tau_c$ of the inverse reduced compressibility $1/\chi_\text{red}$ and of the internal energy per unit volume $u$ is obtained. The reduced pressure and chemical potential outside the region bounded by the spinodal can be determined by integrating $1/\chi_\text{red}$ along the critical isotherm from $\rho_c$ to the desired $\rho$, and then $\partial u/\partial \rho$ along an isochore from $\tau_c$ to the desired $\tau$. As pointed out in the previous section, this procedure is well defined due to the self-consistency of the theory. Once the pressure and the chemical potential are known, the coexistence curve near the critical point is found analytically, along with the critical exponents for $\tau < \tau_c$.

In summary, the constraint of the Ornstein–Zernike ansatz, when combined with the exact constraints of self-consistency and the core condition, is found to give rise to a type of thermodynamic and correlation-length scaling that is somewhat different from the scaling one would expect in an exact treatment of a three-dimensional fluid. The SCOZA scaling functions are relatively simple, giving rise to critical exponents that are integers or ratios of small integers. But these functions differ from form above and below $\tau_c$ more substantially than in an exact description, where the exponents defined above and below $\tau_c$ are expected to coincide.

Figure 5 shows the reduced compressibility of the HCYF for $\tau > \tau_c$ and $\rho = \rho_c$ as a function of the reduced temperature $\tau = (\tau - \tau_c)/\tau_c$ on a log–log plot. Also shown is the corresponding ‘effective exponent’ $\gamma_\text{eff}$ defined as the local slope of the plot. It can be seen that $\gamma_\text{eff}$ eventually saturates at $\gamma = 2$, thus signalling the onset of MSA-like power-law behaviour, but the asymptotic regime can be detected only at a very small reduced temperature ($\tau \sim 10^{-4}$). This is the same scenario found previously in the nearest-neighbour lattice gas. For the HCYF, the crossover is controlled as expected by the inverse range parameter $z$. It has been verified that, as the interaction becomes longer and longer ranged, the asymptotic regime is further pushed to smaller and smaller values of the reduced temperature $\tau$ [34].

4. Conclusion

We have studied the thermodynamics and the phase diagram of the HCYF using both the SCOZA and MC
simulations supplemented by a finite-size scaling analysis. A comparison between theory and simulation results shows that the SCOZA yields both very good overall thermodynamics and a remarkably accurate coexistence curve up to the critical point. The version of the SCOZA considered here takes into account the hard sphere contribution to the direct correlation function outside the repulsive core, and sensibly improves the simplest one-Yukawa version, in which the hard sphere gas is described as in the PY approximation. On the other hand, as stated in section 2, here (as well as in the simpler version just mentioned) consistency has been enforced between the internal energy and the compressibility route, but not between the virial route and either of the above. We think that the further development of making the theory fully self-consistent by taking also the virial route into account is worth pursuing, since we anticipate that the present version of the SCOZA will yield liquid-state pressures from the virial theorem that are not significantly better than those obtained using the virial theorem with the LOGA/ORPA $g(r)$. We defer a detailed examination of this issue to a later study. In this respect it is worth mentioning an issue of the HCYF along the lines considered here [35] where some results for the critical parameters were reported taking into account all the three routes to the thermodynamics although, as explicitly pointed out by the authors, the SCOZA equations were studied in an approximate fashion, and no attempt to determine the phase diagram was made.

Although dealing with a Yukawa potential entails certain analytical simplifications in implementing the SCOZA, such an approach can be applied to any kind of tail potential. It should be pointed out also that the idea of using the requirement of self-consistency to get a closed theory of thermodynamics and correlations is pertinent not only to the realm of simple fluids or lattice gases, but also has proved to be a powerful tool in the study of a system of spins with continuous symmetry [36] and of a site-diluted [37] or random-field [38] Ising model.

D.P. gratefully acknowledges the support of the Division of Chemical Sciences, Office of Basic Energy Sciences, Office of Energy Research, US Department of Energy. G.S. gratefully acknowledges the support of the National Science Foundation. N.W.B. acknowledges support from the EPSRC (Grant Number GR/L91412), and the Royal Society of Edinburgh.

Appendix A

Waisman parameterization of $c_{HS}(r)$

We recall the procedure that allows one to determine analytically the amplitude $\kappa_1$ and the inverse range $z_1$ of the direct correlation function $c_{HS}(r)$ of the hard sphere gas in the Waisman parameterization (7). The relevant equations are reported in [21]. Both $z_1$ and $\kappa_1$ are conveniently expressed in terms of two quantities $V_0, V_1$ which are formally analogous to $U_0, U_1$ and $W_0, W_1$ introduced in equations (14) and (15). From [21] equation (2.32a) it is found that $z_1$ is given by

$$z_1 = \frac{2}{q} - f_2 \left\{ \left[ \frac{V_0 + f^2 - q}{f_0} \right] + \left[ \frac{V_0 + f^2 - q}{f_0} \right] \right\}^{1/2},$$

(A 1)

where $f$ and $q$ are defined in equations (10) and (13). The expression of the amplitude $\kappa_1$ is the same as in equation (22) with $U_0, U_1$ replaced by $V_0, V_1$:

$$\kappa_1 = \frac{2(z_1 + 2)^2 \sigma_1^2}{3 \xi_1^2} \left[ \frac{V_1}{V_0} - \alpha_l \right]^2,$$

(A 2)

where $\xi_1 = \pi \sigma_1^2/6$ is the packing fraction and $\alpha_l$ is a function of $z_1$ given by equation (23). The ratio $V_1/V_0$ can be expressed as a function of $V_0$ by [21] equations (2.24) and (2.26). One has

$$\frac{V_1}{V_0} = 2 - q^{1/2} - \frac{1}{2 V_0 q^{1/2}} \left[ (V_0 + f^2 - q)(V_0 + f^2) \right]
+ \frac{1}{4 z_1^2} (q - f^2) \right]$$

(A 3)
To obtain the explicit expressions of \( z_1 \) and \( \kappa_1 \) as functions of the density, one must then feed into equations (A 1)–(A 3) the expression for \( v_0 \). This depends on the contact value of the radial distribution function \( y_0 \equiv g(r = 1^+) \) via [21] equation (2.32b),

\[
 v_0 = 6\xi_0 - f^2 + 1.
\]  

(A 4)

For a hard sphere gas \( y_0 \) can be determined from the equation of state via the virial equation

\[
 \frac{B\rho}{\rho} = 1 + 4\xi_0.
\]  

(A 5)

The requirement that both the virial and the compressibility route to the thermodynamics must give the Carnahan–Starling equation of state is then satisfied if the Carnahan–Starling pressure and compressibility are substituted, respectively, in equation (A 5) and equation (10). Equations (A 4) and (A 3) then yield \( v_0 \) and \( v_1/v_0 \) as functions of density. From equations (A 1) and (A 2) we finally obtain \( z_1 \) and \( \kappa_1 \).

### Appendix B

#### Simulation details

The principal aspects of the simulation and finite-size scaling techniques employed in this work have been detailed elsewhere in the context of a similar study of the Lennard-Jones fluid. Accordingly we confine our description to the barest essentials and refer the reader to [16] for a fuller account of our methods.

The Monte-Carlo simulations were performed using a Metropolis algorithm within the grand canonical ensemble [39]. The MC scheme comprises only particle transfer (insertion and deletion) steps, leaving particle moves to be performed implicitly as a result of repeated transfers. To simplify identification of particle interactions a linked-list scheme was employed. This involves partitioning the periodic simulation space of volume \( L^3 \) into \( m^3 \) cubic cells, each of side the cutoff \( r_c \). This strategy ensures that interactions emanating from particles in a given cell extend at most to particles in the 26 neighbouring cells.

In our Yukawa system the potential was cut off at a radius \( r_c = 3.0\sigma \), and a correction term was applied to the internal energy to compensate for the truncation. System sizes having \( m = 3, 4, 5, 6 \) and 7 were studied, corresponding (at coexistence) to average particle numbers of approximately 230, 540, 1050, 1750 and 2900, respectively. For the \( m = 3, 4 \) and 5 system sizes, equilibration periods of \( 10^5 \) Monte Carlo transfer attempts per cell (MCS) were utilized, while for the \( m = 6 \) and \( m = 7 \) system sizes up to \( 2 \times 10^6 \) MCS were employed. Sampling frequencies ranged from 20 MCS for the \( m = 3 \) system to 150 MCS for the \( m = 7 \) system. The total length of the production runs was also dependent upon the system size. For the \( m = 3 \) system size, \( 1 \times 10^7 \) MCS were employed, while for the \( m = 7 \) system, runs of up to \( 6 \times 10^7 \) MCS were necessary.

In the course of the simulations, the observables recorded were the particle number density \( \rho = N/V \) and the energy density \( u = E/V \). The joint distribution \( p_M(\rho, u) \) was accumulated in the form of a histogram. In accordance with convention, we express \( \rho \) and \( u \) in reduced units: \( \rho^* = \rho\sigma^3 \), \( u^* = u\sigma^3 \). To allow us to explore efficiently the phase space of the model, we employed the histogram reweighting technique [40]. This method allows a histogram accumulated for one set of model parameters to be reweighted to provide estimates appropriate for another set of not-too-distant model parameters.

To facilitate the study of the subcritical coexistence region, the multicanonical preweighting technique [41] was employed. This technique allows one to circumvent the problems of metastability and non-ergodicity that otherwise would arise from the large free energy barrier separating the coexisting phases. Details of this technique and its implementation in the fluid context are described in [16].

The critical point parameters were estimated using finite-size scaling technique as described in [16]. This involves matching the distribution function of the ordering operator to the independently known universal critical point form appropriate for the Ising universality class. The ordering operator is defined as \( M \propto (\rho^* + su^*) \), where \( s \) is a non-universal ‘field mixing’ parameter, which is finite in the absence of particle–hole symmetry, and which is chosen to ensure that \( \rho(M) \) is symmetric in \( M \). However, the estimate of the apparent critical tem-
temperature obtained by this matching procedure is subject to errors associated with corrections to finite-size scaling. To deal with this, we extrapolate to the thermodynamic limit using the known scaling properties of the corrections, which are expected to diminish (for sufficiently large system sizes) as $L^{-\theta/\nu}$ [16] where $\theta$ is the correction to scaling exponent and $\nu$ is the correlation length exponent. The extrapolation has been performed using a least-squares fit to the data for the four largest system sizes. The results of the extrapolation are shown in figure B1, from which we estimate $\tau_c = 1.212(2)$. The associated estimate for the critical density is $\rho_c^* = 0.312(2)$.

References


